

Statistical Thermodynamics in Chemistry and Biology

22. Electrochemical equilibria

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Electrochemical equilibria

This chapter:

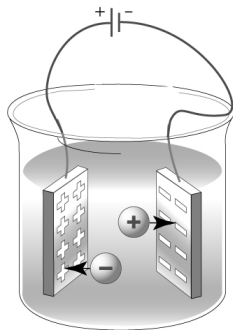
- ▶ Introduction to electrochemistry
- ▶ Combine the laws of electrostatics and (statistical) thermodynamics

Adding ions to the fundamental equation

- ▶ The internal energy, U , is a function of the **extensive** variables $U(S, V, \mathbf{N})$, which is now extended with the charges, \mathbf{q} of the system: $U(S, V, \mathbf{N}, \mathbf{q})$.
- ▶ The electrostatic potential, $\psi(x)$, **depends on the spatial coordinate x** , i.e. in between the electrodes in an electrochemical cell (see figure).
- ▶ Divide the coordinate x into M finite segments x_i , where N_i is the number of molecules in segment i and q_i is the amount of charge in segment i , respectively.
- ▶ The fundamental equation for U , (including only one component):

$$dU = TdS - pdV + \sum_{i=1}^M \mu_i dN_i + \sum_{i=1}^M \psi_i dq_i$$

where the sum runs over the number of segments M .



Adding ions to the fundamental equation

Part 2

- ▶ The Gibbs free energy, ($G = U + pV - TS$):

$$dG = -SdT + Vdp + \sum_{i=1}^M \mu_i dN_i + \sum_{i=1}^M \psi_i dq_i$$

i.e. molecules dN_i and charge dq_i will move along the x-coordinate (between the segments) until equilibrium is reached ($dG = 0$).

- ▶ For molecular ions, $q_i = zeN_i$, where z is the ion charge in unit charges of e , (electron charge: $-e$)

$$dG = -SdT + Vdp + \sum_{i=1}^M (\mu_i + ze\psi_i) dN_i$$

Adding ions to the fundamental equation

Part 3

- ▶ The **electrochemical potential** is defined as

$$\mu'_i = \mu_i + z_i e \psi_i$$

so that

$$dG = -SdT + Vdp + \sum_{i=1}^M \mu'_i dN_i$$

- ▶ At constant p and T , equilibrium occurs when the **electrochemical potential is equal everywhere**, e.g.

$$\mu'_1 = \mu'_2 \quad \Leftrightarrow \quad \mu'(x_1) = \mu'(x_2)$$

- ▶ An example of a **general approach** to extend thermodynamics with an extra energy term, where the additional energy term depends on the **spatial coordinate**.

The Nernst equation

- ▶ For a **single ionic species**, the condition for equilibrium is

$$\mu'(x_1) = \mu'(x_2)$$

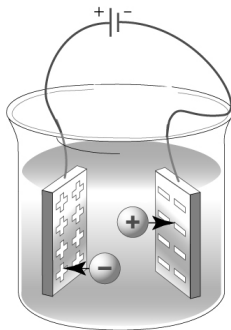
- ▶ Using $\mu(x) = \mu^o + k_B T \ln c(x)$, (for an ideal solution) gives for the electrochemical potential,

$$\mu'(x) = \mu^o + k_B T \ln c(x) + ze\psi(x)$$

- ▶ At equilibrium,

$$\ln \frac{c(x_2)}{c(x_1)} = \frac{-ze(\psi(x_2) - \psi(x_1))}{k_B T}$$

which is the **Nernst equation**



The Nernst equation

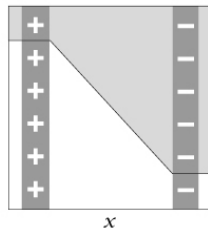
Part 2

- Alternatively (see figure when ψ is a linear function in x),

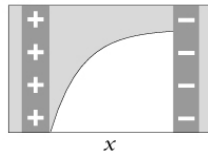
$$c(x_2) = c(x_1) e^{\frac{-ze(\psi(x_2) - \psi(x_1))}{k_B T}}$$

- Note that **electroneutrality is a very strong macroscopic condition**. Whereas the chemical potential μ measures the free energy difference to insert a particle, the electrochemical potential measures the free energy difference of inserting an electroneutral ion pair.

(a)

 $\psi(x)$ 

(b)

 $c_+(x)$ 

Neutral salts

- ▶ For a salt, e.g. NaCl, that ionizes,

$$\mu_{\text{NaCl}} = \mu'_{\text{Na}^+} + \mu'_{\text{Cl}^-}$$

- ▶ or

$$\mu_{\text{NaCl}} = \mu_{\text{Na}^+}^o + k_B T \ln c_{\text{Na}^+} + e\psi_{\text{Na}^+} + \mu_{\text{Cl}^-}^o + k_B T \ln c_{\text{Cl}^-} - e\psi_{\text{Cl}^-}$$

- ▶ If ψ is spatially uniform, $\psi_{\text{Na}^+} = \psi_{\text{Cl}^-}$,

$$\mu_{\text{NaCl}} = \mu_{\text{NaCl}}^o + 2k_B T \ln c_{\text{NaCl}}$$

where the standard chemical potentials have been grouped together, and $c_{\text{NaCl}} = c_{\text{Na}^+} = c_{\text{Cl}^-}$.

On the relationship between the chemical potential and the equilibrium constant

A recapitulation of previous material

- For the reaction,



we had at equilibrium (Eq. 13.16),

$$c\mu_C = a\mu_A + b\mu_B$$

- For an ideal solution,

$$\mu_A = \mu_A^o + k_B T \ln[A]$$

where we equally well can express μ_A in terms of the concentration $[A]$ as in terms of the molar fraction, x_A .

On the relationship between the chemical potential and the equilibrium constant

Part 2

- ▶ For the reaction (at equilibrium),

$$c\mu_C^o - a\mu_A^o - b\mu_B^o = -k_B T (c \ln[C] - b \ln[B] - a \ln[A]) = -k_B T \ln \frac{[C]^c}{[A]^a[B]^b}$$

- ▶ Rewritten as,

$$\mu_{\text{liquid}}^o = -k_B T \ln K_C$$

or in general (not assuming equilibrium),

$$\mu_{\text{liquid}} = \mu_{\text{liquid}}^o + k_B T \ln \frac{[C]^c}{[A]^a[B]^b} = \mu_{\text{liquid}}^o + k_B T \ln Q$$

where K_C is the equilibrium constant expressed in concentrations and Q is the reaction quotient also expressed in concentrations. At equilibrium $Q = K_C$ and $\mu_{\text{liquid}} = 0$.

The Nernst equation for an electrode

Phrased slightly different as compared to the book

- ▶ Consider a reaction, $M^{z+} + ze^{-} \rightarrow M$
- ▶ Condition for equilibrium,

$$\mu'_{\text{solid}} = \mu'_{\text{liquid}}$$

- ▶ For the liquid,

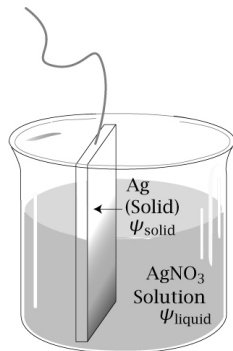
$$\mu'_{\text{liquid}} = \mu_{\text{liquid}}^{\circ} + k_B T \ln Q + ze\psi_{\text{liquid}}$$

and for the solid,

$$\mu'_{\text{solid}} = \mu_{\text{solid}}^{\circ} + ze\psi_{\text{solid}}$$

- ▶ At equilibrium,

$$\mu_{\text{liquid}}^{\circ} + k_B T \ln Q + ze\psi_{\text{liquid}} = \mu_{\text{solid}}^{\circ} + ze\psi_{\text{solid}}$$



The Nernst equation for an electrode

Part 2

- ▶ The unmeasurable materials properties are grouped together,

$$ze\psi_0 = \mu_{\text{solid}}^o + ze\psi_{\text{solid}} - \mu_{\text{liquid}}^o$$

where ψ_0 is termed the **half-cell potential** and is a property of the electrode reaction (and can be found in tables).

- ▶ Thus,

$$ze\psi_{\text{liquid}} = ze\psi_0 - k_B T \ln Q$$

- ▶ Using the definition for **Faraday's constant**, $F = N_A e$ and $R = N_A k_B$,

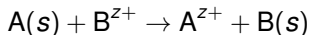
$$\psi_{\text{liquid}} = \psi_0 - \frac{RT}{zF} \ln Q$$

which is more general than eq. (22.18), but in principle the same.

The Nernst equation for an electrochemical cell

The combination of two electrodes (not in the book)

- ▶ Consider the cell reaction,



- ▶ The potential difference, $\Delta\psi$, between two electrodes, A and B , in a cell becomes

$$\Delta\psi = \psi_{0,B} - \psi_{0,A} - \frac{RT}{zF} \ln Q$$

- ▶ The half-cell potentials are measured relative to each other, and the hydrogen electrode is used as the reference $\psi_{0,H_2} = 0 \text{ V}$.
- ▶ Example: What is the half-cell potential for the following reaction $Zn^{2+} + 2e^- \rightarrow Zn(s)$?
 - ▶ Given: The half-cell potential for $Cu^{2+} + 2e^- \rightarrow Cu(s)$ is 0.34 V.
 - ▶ Given: The potential difference in the cell for $Zn(s) + Cu^{2+} \rightarrow Cu(s) + Zn^{2+}$ is measured to 1.10 V at standard conditions (i.e. the concentrations are 1 M).
 - ▶ The cell reaction is obtained by the given half-cell reaction minus the requested half-cell reaction: $1.10 = 0.34 - \psi_{0,A}$, which gives a half-cell potential of -0.76 V .

Summary

- ▶ An introduction to electrochemistry: **Nernst equation**
- ▶ Example of how to add an extra energy term to thermodynamics.
- ▶ Introduced how to treat energies/potentials that depend on the **spatial coordinate**.
- ▶ Introduced **half-cell potentials** and **Nernst equation for an electrode**.

E22:2 (Exam Dec.-2008:3)

- a) Describe in a few sentences what the chemical potential is. If we have ions in the solution, what is the electrochemical potential?
- b) We have a container with SF_6 gas with the height, $h_0 = 50$ cm. Include the effect of gravitation in the Gibbs free energy, and derive an expression for the concentration dependence on the container height, $c(h)$, at constant pressure and temperature. Is the concentration highest at the top or at the bottom of the container? Is the concentration gradient significant for molecular systems? The temperature is 300 K. (Atomic masses: $m_S = 32.06$ g/mol; $m_F = 18.99840$ g/mol)